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A STUDY OF SULPHUR ALLOTROPES BY THE X-RAY DIFFRACTION METHOD *

PART I

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Plates IV and V.

ABSTRACT. The structures of the various modifications of sulphur at temperatures ranging between $-183°C$ and $130°C$ have been investigated by Hull's diffraction method. The following important observations and conclusions have been made.

1. Ordinary roll sulphur and flower of sulphur have identical crystalline structures similar to that of the orthorhombic sulphur (S_α).

2. Milk of sulphur and the gummy deposits of colloidal sulphur which are insoluble in CS_2 and regarded as amorphous, are really crystalline. Their patterns clearly indicate that they are identical in structure with S_α.

3. Plastic sulphur when freshly prepared by pouring boiling sulphur in cold water, is really amorphous, producing only one diffuse band ($d = 3·5$ Å). It rapidly transforms into a hard solid mass insoluble in CS_2, which has a structure similar to that of S_α. When kept at a high temperature (about 60° C), or treated with strong NH_4OH the substance becomes soluble in CS_2

4. White sulphur obtained by the hydrolysis of S_2Cl_2, hitherto supposed to be amorphous, has exhibited a well-defined crystalline pattern, quite different from that of S_α. It is insoluble in CS_2. When heated for some time at about 88°C, it transforms entirely and permanently into S_α

5. The insolubility of the various forms of sulphur has been suggested to be, some way, due to the presence of SO_2 on the surface of the crystallites.

6. The special features characterising the patterns obtained at temperatures lying between 80°C and 110°C are : (*a*) the discontinuity of the rings, (*b*) the appearance of asterism, *i. e.*, radial streaks, and (*c*) the appearance of a large number of sharp intense spots arranged irregularly on the plate. It has been shown that the changes noticed in the pattern are due to the growth of the crystal size in the heated exposed specimens of powdered sulphur (S_α), and have nothing to do with the enantiotropic transformation of S_α into S_β which is generally known to take place at 95·5° C or above.

7. All attempts in recording a pattern of S_β failed probably due to (*a*) the instability of S_β at the ordinary room temperature and (*b*) the growth of crystal-size and the disfiguration of the patterns at higher temperatures where S_β is stable.

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8. Patterns of liquid sulphur have been obtained at 114°C, 119°C and 128°C, and in each case two bands have been obtained.

9. No appreciable change in the pattern has been observed at as low a temperature as −183°C.

INTRODUCTION

An extensive Physico-Chemical study of sulphur led to the discovery of a large number of its allotropes, both crystalline and amorphous. Though the multifarious complexities of the element have been engaging the time and attention of a large number of investigators who in gradual steps, have explicated some of the multifold peculiarities of sulphur, still there are many interesting but obscure points awaiting plausible explanations and demanding a systematic investigation on the subject. The representation made here describes the results obtained by the present author during the course of a systematic study of the various modifications of sulphur, under different physical conditions by the X-ray method.

A brief outline of our present knowledge of sulphur and its allotropes concerning the subject-matter of the present investigation is stated below.

1. SULPHUR AND ITS ALLOTROPES

(a) *Orthorhombic sulphur*[1] (S_α)

Ordinary roll sulphur and almost the whole of the flower of sulphur belong to this class. Sulphur crystallised from a cold solution in CS_2 also forms a orthorhombic system. This variety has been analysed by the X-ray method by Bragg,[2] Mark and Wigner,[3] and Warren and Burwell.[4] The final result obtained from these analyses indicates a space group $V_2^h{}_1$. The size of the unit cell is found to be, $a = 10{\cdot}48$, $b = 12{\cdot}92$ and $c = 24{\cdot}55$ in Angstrom units. Each cell contains sixteen S_8 molecules or 128 atoms. This variety of crystalline sulphur is stable at the ordinary temperature.

(b) *Monoclinic sulphur* (S_β)[5,18]

Several varieties of monoclinic sulphur have been observed and described by the crystallographers but amongst them, the needle shaped crystal obtained from molten sulphur is the most common type. It is very unstable below 95°·5 C and is reported to be stable above this temperature. S_α and S_β are known as enantiotropic, the accepted value of the transition temperature corresponding to $S_\alpha \rightleftharpoons S_\beta$ is 95°·5 C. Orthorhombic sulphur is stable below and unstable above this temperature. No X-ray analysis of S_β has yet been attempted.

(*c*) *The amorphous allotropes of sulphur*

These amorphous allotropes of sulphur are obtained only by very special means. The well known varieties are : (*i*) Milk of sulphur,[6] (*ii*) Colloidal sulphur,[7] (*iii*) White sulphur,[8] and (*iv*) Plastic sulphur.[9] J. J. Trillat and J. Forestier [10] have analysed this substance after stretching its thread from 8 to 10 times its original length. They have concluded that the substance is crystalline and the axial lengths are different from those of S_α. Plastic sulphur under ordinary conditions is known as amorphous, but it quickly solidifies into a hard mass consisting of S_α and S_μ. S_α is soluble in CS_2 and crystalline, while S_μ is insoluble in CS_2 and amorphous.[9]

(*d*) *Liquid sulphur*

The accepted values of the melting points* of pure S_α and of pure S_β are 113°·0 C and 119°·4 C respectively.[11] But here also the opinions of the different authors vary widely. The liquid sulphur is supposed to contain two types of sulphur S_λ (soluble in CS_2) and S_μ (insoluble in CS_2) and the proportion of the latter increases with the temperature. If a quantity of molten sulphur is allowed to solidify, the proportion of soluble and insoluble sulphur in the solid depends on the relative amounts of S_λ and S_μ present in the liquid at the time of solidification.[9] The plastic sulphur which is prepared by pouring boiling sulphur into cold water is also sometimes called a super-cooled type of S_μ[9].

Blatchford [12] has studied liquid sulphur at temperatures ranging from 130°C to 210° C by the X-ray diffraction method. From the experimental results he concludes that the sulphur molecules have a more or less regular grouping amongst them and further the spacing corresponding to the diffraction ring does not conform to the close packing theory. At about 180° C he has observed a sudden change in the value of the spacing which is correlated with the well known change of viscosity of the fluid at a neighbouring temperature.

2. EXPERIMENTAL

The powder photograph method is chiefly adopted in the present investigation. The slit system (fig. 1) is of special design. It behaves both as a slit and also as a supporter of the specimen under examination. It consists of a thick-walled brass tube A, $\frac{3}{4}$" in outer and $\frac{1}{4}$" in inner diameter, and 8 c.m. in length. The tube is closed at the ends by means of two brass plugs B and C. The plug B on the tube-side of the slit has a bore of 1 m.m. co-axial with the main tube A, while C lying on the plate-side has a bore of 0·4 m.m. In

* The values of the m. pts of sulphur as recorded by different authors widely vary. For rhombic sulphur it varies between 112°·8 C (Partington, A Text Book of Inorganic Chemistry, 1938, p. 488), and 119°·25 C (Mellor, Modern Inorganic Chemistry, 1919, p. 400).

order to protect the plate from the rays scattered by the slit, a shield-tube D is screwed on to A against C at the plate-end of the slit.

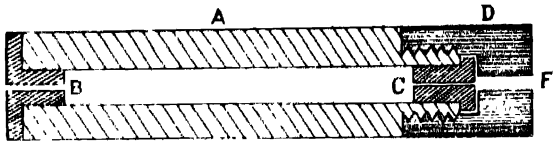


FIGURE 1.

The cell containing the diffracting material of proper thickness was placed in direct contact with the face of the shield D at F by means of a washer and a couple of screws. The shield D, along with the cell is easily demountable and serves another important purpose, *i.e.*, during the exposure on the same plate, the cell can easily be re-filled by the diffracting material at any desired interval of time. This device is of great assistance when one has to examine by X-ray diffraction, some volatile substance, or an unstable substance which is liable to change its modification under the experimental conditions specially when the rate of transformation is very rapid. It is convenient in such cases to have two exactly similar detatchable shields, so that one of them may be kept ready in hands with the refilled cell immediately before the first cell is required to be withdrawn. The second cell is then put before the slit system, thus saving considerable amount of time.

For investigating the material kept at a high temperature during the exposure, an electric heater was employed, where any particular temperature measured by a thermocouple, could easily be maintained within 2° C, by sliding resistances. A cylindrical Cyndanio bobbin coiled with nichrome wire formed the simple heater, and the axial bore of the bobbin exactly fitted the slit tube.

The experiments with sulphur S_α at lower temperatures were conducted with carbon dioxide snow, liquid oxygen, etc., and a special vacuum chamber was constructed for this purpose ; but the present paper records only results of preliminary experiments, so far as the low temperature works are concerned and a full description of the apparatus is deferred at the present moment. The various forms of sulphur used in the present investigation were prepared by the author in this laboratory. The chemicals used for the purpose were either the preparations of E. Merck or of Schering Kahlbaum.

3. RESULTS

A. *Orthorhombic sulphur (Fig. 4)* *

Fine powders of roll sulphur, flower of sulphur and sulphur recrystallised

* The distance between the cell and the photographic plate is different for different photographs. For figures 2, 3 and 4 the distance R is 2·452 c. m. for figures 5, 6, 7, 10, 13 and 14, R is 1·965 c. m. for figures 8, 9 and 12, R is 2·248 c. m. ; for figure 11, R is 2·370 c. m. In the final print, the figures are reduced to three-fourth of the original size.

Fig. 2.

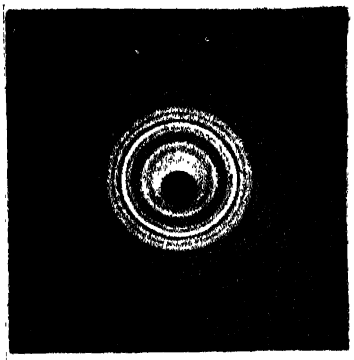


Fig. 3.

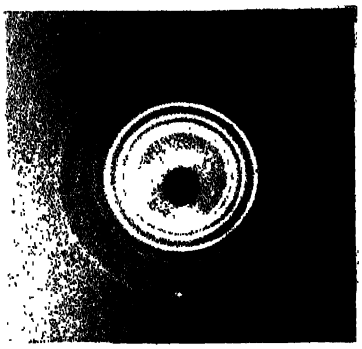


Fig. 4.

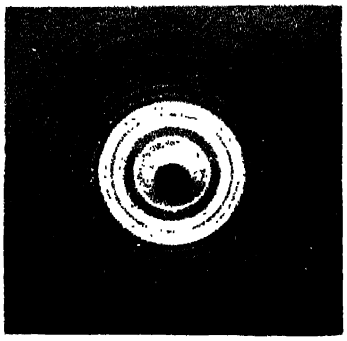


Fig. 5

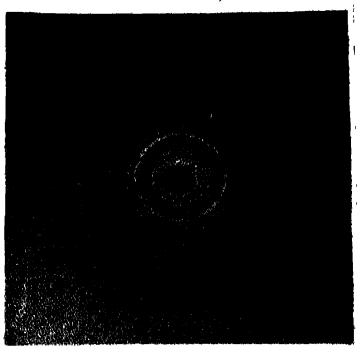


Fig. 6.

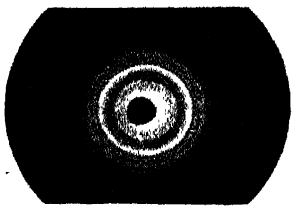
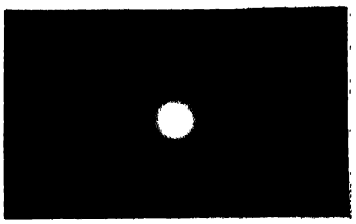


Fig. 7.



Powder diagrams.

Fig. 2 White sulphur after heating at 88° C.
Fig. 3.– White sulphur.
Fig. 4 —Recrystallised sulphur.
Fig. 5.– Hardened plastic sulphur rendered soluble by NH_4OH.
Fig. 6.– Hardened insoluble plastic sulphur.
Fig. 7.– Colloidal deposit of sulphur.

from a solution in CS_2 were examined. These forms of sulphur are known to belong to the rhombic type of crystals. The diffraction patterns obtained in these cases also support this view. For, the values of the Bragg-spacings and the intensities of the corresponding rings in the patterns of the different members closely agree with one another.

B. *Milk of sulphur (Fig. 1d)*

This is one of the well known varieties supposed to be amorphous. To a freshly prepared solution of calcium polysulphide, dilute acid (1 acid 1 water) was gradually added, when a milky white precipitate with slightly yellowish tinge was obtained. Two different samples of this variety were prepared by acidulating with (*a*) dil. HNO_3 and (*b*) dil. HCl. These varieties are found to exist in a state of extremely fine division and were exposed to X-ray without any artificial powdering. The ring systems of the two samples are similar to each other and also to that of orthorhombic sulphur S_α. The sharpness and the continuity of the rings produced by milk of sulphur clearly indicate that the sizes of these minute crystals lie between 10^{-3} to 10^{-5} c.m. in each direction. Thus we find that milk of sulphur is not really amorphous, but is crystalline and the structure is exactly similar to that of the orthorhombic α-sulphur. During the precipitation of milk of sulphur, the colour of the precipitate appeared perfectly milk-white immediately after its formation, but very soon turned slightly yellowish. This was evidently due to the conglomeration of white smaller particles into bigger ones which are generally yellow.

C. *Colloidal sulphur*

This modification of sulphur was prepared in the state of colloidal suspension in water, by passing pure H_2S through a concentrated solution of SO_2 in water at about 5°C – 10°C. The colloidal solution obtained in this way was filtered twice and preserved. Deposition of gummy solid sulphur took place from this solution spontaneously but the rate was extremely slow. The colour of a concentrated solution of colloidal sulphur appears yellow by reflected light, but deep reddish brown by transmitted light. The yellow colour gradually gets fainter and finally disappears with the increase of dilution; but at a certain stage, the reflected colour becomes bluish, while the colour of transmission still remains brown. To a quantity of the colloidal solution, we added a strong solution of NH_4OH * which coagulates the colloidal particles, and the deposits

* It is a well-known fact that a suitable electrolyte may deposit particles held in colloidal suspension. The special reason for selecting NH_4OH in the present case was that it could be driven out of the deposit by simple evaporation.

formed by spontaneous sedimentation and by the addition of NH_4OH were analysed by X-rays.

The diffraction rings obtained in the cases of these two types of colloidal deposits of sulphur are exactly similar to those of S_α. The rings are quite sharp but are slightly broader than the corresponding rings of orthorhombic sulphur. This fact naturally suggests that the particles in colloidal deposits are very small so that sufficient number of lattice planes are not available for the production of sharp rings.[13,14] Similar observations have been made by many observers in the cases of colloidal particles of metals,[15,16] which on analysis have exhibited their crystalline structures. Colloidal particles of sulphur are therefore not amorphous but consist of extremely minute crystals of the orthorhombic type (S_α).

We made an attempt to obtain the diffraction patterns of the colloidal sulphur particles in their state of suspension in water. But so far no ring system of sulphur was observed. Only a wide band due to water appeared in the photographs.*

D. *Plastic sulphur (Fig. 13)*

This is the widely known amorphous allotrope of sulphur.[9] We prepared it by pouring boiling sulphur into cold water in thin streams. A highly sticky deep-brown (almost black) substance was obtained. A small quantity of this substance was laid in a thin layer on a piece of very thin paper by means of a clean glass rod. The film was then applied on the carrier as described in previous sections.

Plastic sulphur is known to be highly unstable under ordinary laboratory conditions. For this reason in the present investigation the specimen of plastic sulphur was replaced at an interval of one hour during the exposure. Several photographs were taken in this way and the pattern obtained in each case consisted of a single diffuse band corresponding to the Bragg spacing 3·5 A. In one case we allowed the one and the same specimen to be exposed for about 4 hrs. and the photograph obtained consisted of several faint but sharp rings like those of S_α. This, therefore shows that plastic sulphur had considerably transformed into S_α within four hours. Plastic sulphur as it is produced is really amorphous and the present work shows that it is the only amorphous form of sulphur. J. J. Trillat and J. Forestier[10] have analysed a thread of plastic sulphur after extending it, by longitudinal tension, from 8 to 10 times its original length. The photograph revealed a fibre-pattern. From this they have come to the conclusion that the substance is crystalline. The identity period in the direction

* Recently with improved technique, the ring systems of sulphur particles suspended in water has been studied.

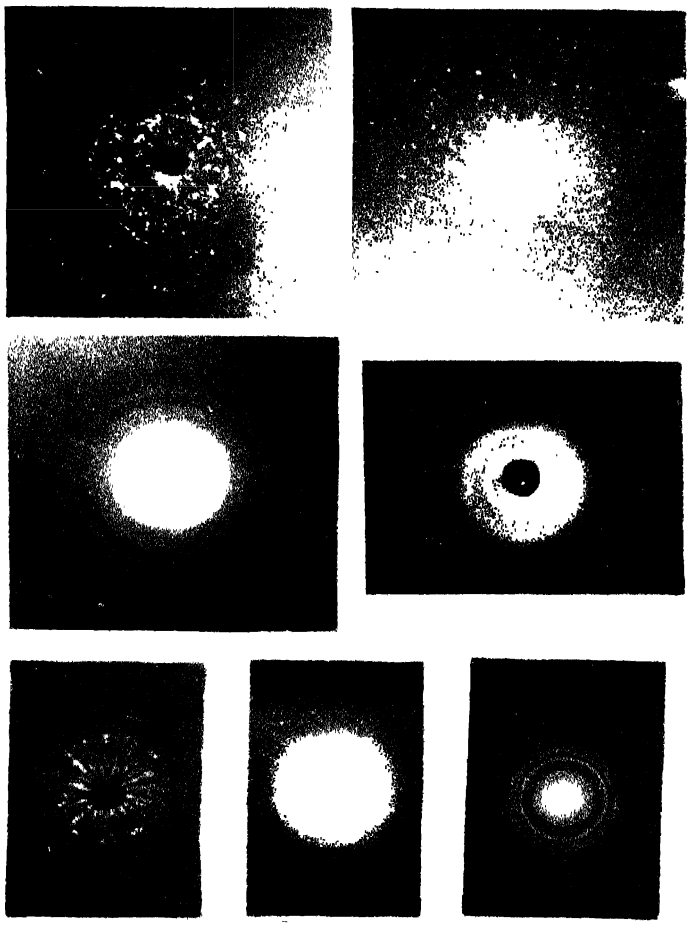


Fig. 8. Fig. 9.

Fig. 10. Fig. 11.

Fig. 12. Fig. 13. Fig. 14.

Powder diagrams.

Fig. 8.—Sulphur heated at 104° C for 40 hours.
Fig. 9.—Sulphur heated at 104° C for 60 hours.
Fig. 10. Sulphur in collodion at 104° C.
Fig. 11.—Liquid sulphur at 117° C.
Fig. 12.—Sulphur heated at 104° C for 10 hours.
Fig. 13.—Fresh plastic sulphur.
Fig. 14.—Milk of sulphur.

of the fibre is found to be equal to 9.35 Å which approximates to the length of the a-axis (10·61 Å) of S_α. This observation admits of two explanations: (1) As plastic sulphur is extremely unstable it is mostly converted during the time of exposure (6 hrs.) into the orthorhombic crystallites which, under the force of tension, oriented with their a-axis more or less parallel to the applied force. This certainly can not adequately account for the considerable shortening (about 12·5%) of the a-axis of fibrous plastic sulphur. (2) Another explanation to which we may direct our attention, depends upon a possible similarity between a thread of plastic sulphur and a piece of rubber. The latter though amorphous under ordinary conditions, produces a fibre pattern, when extended by tension and the sharpness of the pattern increases with the degree of extension.[20, 21, 25] This behaviour of rubber is satisfactorily explained by the supposition of the preferred orientation of the highly polymerised isoprene (C_5H_8) molecules present in it. In the case of plastic sulphur we may well assume that the S_8 molecules or any higher complex present in it may behave exactly in the same way as the molecules of rubber. But a clear unambiguous explanation requires further investigations.

F. *Hardened plastic sulphur (Fig. 6).*

It has been mentioned that plastic sulphur solidifies into a very hard and brittle grey mass when kept for a few hours at ordinary temperatures.[9] We have observed that the transformation into the solid state is accelarated by the elevation of temperature (70°C – 100°C), but the solid in the latter case does not become so hard. It becomes, rather friable and falls to powder even by the pressure of the fingers. There is another difference in the two types of solidified plastic sulphur, the hard variety (formed at the room temperature) is almost entirely insoluble whereas the second variety (formed at 70° C – 100° C or above) is completely soluble in CS_2. Both the soluble and the insoluble specimens produce exactly similar patterns, the inner rings of the insoluble specimen are slightly diffuse (Fig. 6).

The coarsely powdered insoluble variety as well as the thin film of hardened plastic sulphur produced identical patterns, resembling those of the thoroughly powdered specimen. This also shows that the crystal grains in the insoluble specimens are extremely small. But the specimen soluble in CS_2 behaved in a quite different manner. The diffraction rings in this case ceased to be uniform when the powder was coarse, indicating that heat had caused a growth of the micro-crystals. We have observed a similar phenomenon of growth at higher temperature in the case of ordinary sulphur, which will be described in a later section.

F. *Hardened plastic sulphur rendered soluble by NH_4OH (Fig. 5)*

A quantity of the hard insoluble mass was thoroughly powdered and kept in a stoppered bottle containing a strong solution of ammonia. After three days we examined the powder which was first thoroughly washed and desiccated. It became almost completely soluble in CS_2 and the diffraction pattern obtained in this case was free from the diffuseness which was observed in the case of the untreated specimen. The powders required no further powdering for the production of continuous rings, indicating that no growth of the crystal size had taken place. This observation is of much importance inasmuch as it helps us to understand the exact nature of the plastic sulphur. The observed diffuseness of the rings of the insoluble specimen was first assumed to be due to the joint actions of the probable distortion of the crystal lattice formed by sudden cooling and to the extreme smallness of their sizes. This idea was further strengthened by the fact that the insoluble specimen when heated not only shows clear signs of crystal growth but also gives rise to a system of sharp rings under proper conditions.

This idea had to be modified. For, we can conceive of no mechanism by which NH_4OH can bring about a growth of the crystal size. Therefore, the diffuseness of the rings produced by insoluble solidified plastic sulphur must be due to some other factor.*

G. *Solubility and insolubility of sulphur*

Table (I) briefly summarizes our knowledge about the point. From a study of the table we can generalise that whenever an insoluble variety of sulphur is produced, SO_2 is always present in the reactions involved This naturally suggests that insolubility may be due to the presence of SO_2 which forming a shielding layer on the surface of the small crystal grains prevents them from coming in contact with the solvent. This idea is further corroborated by solubility of solidified plastic sulphur which has been treated with NH_4OH or has been heated to a high temperature. The latter possibly drives out and the former chemically reacts with the SO_2 gas and thus in both the cases the sulphur grains are rendered free from the SO_2 layer and the solubility is restored.

* Recently the problem of solubility or insolubility of the various types of sulphur has been carefully studied and the results will be published later.

TABLE I.

The solubility or insolubility of the different types of sulphur in carbon disulphide.

	The variety of sulphur.	Structure.	Nature	Chemical reactions in preparations.
1	Roll sulphur ...	S_α	soluble	
2	Flower of sulphur (Merck) .	S_α	soluble	
3	Milk of sulphur ...	S_α	soluble	$CaS_x + 2HCl = CaCl_2 + xS$.
4	Colloidal sulphur ...	S_α	insoluble	$2H_2S + SO_2 = 3S + 2H_2O$.
5	White sulphur ...	S_ω	insoluble	$S_2Cl_2 + 2H_2O = 3S + SO_2 + 4HCl$.
6	White sulphur heated to 88°C ...	S_α	soluble (partly)	
7	Fresh plastic sulphur ...	amorphous	insoluble	Boiling S suddenly poured in cold water. (S burns in air to SO_2.)
8	Hardened plastic sulphur .	S_μ	insoluble	
9	Hardened plastic sulphur heated to a high temperature, or treated with a strong solution of NH_4OH.	S_α	soluble	
10	Monoclinic sulphur ...	S_β	soluble	

The following table II shows the Bragg-spacings of (*a*) roll sulphur, (*b*) flower of sulphur, (*c*) recrystallised sulphur, (*d*) milk of sulphur, (*e*) colloidal sulphur and (*f*) insoluble hardened plastic sulphur. The lattice planes producing the rings have been identified by using Warren and Burwell's [4] values of the dimensions of the unit cell of orthorhombic sulphur. The Millerian indices of these planes are given in the ninth column.

TABLE II.

Obs. spacings $\times 10^8$.	Intensity.	Roll sulphur.	Flower of sulphur	Recrystallised sulphur.	Milk of sulphur.	Colloidal sulphur.	Hardened plastic S.	Indices of the planes.	Calc. spacings $\times 10^8$.
d_1	m.s.	5·66	5·66	5·66	5·66	5·66	5·60	032	5·71
d_2	v.s.	3·84	3·85	3·84	3·84	3·84	3·84	232	3·84
d_3	s.	3·45	3·45	3·45	3·45	3·45	3·48	026	3·45
d_4	s.	3·14	3·14	3·14	3·15	3·14	3·14	216	3·13
d_5	m.s.	2·85	2·84	2·84	2·86	2·83	2·82	044	2·85
d_6	w.	2·64	2·64	2·64	2·63		2·63	400	2·65
d_7	v.w.	2·41	2·40	2·41			2·41	404	2·41
d_8	w.	2·25	2·24	2·26					
d_9	v.w.	2·12	2·12	2·12	2·12		2·11	062	2·12
d_{10}	v.w.	1·98	1·98	1·98			1·99	441	1·99
d_{11}	v.v.w.			1·91			1·90	264	1·89
d_{12}	v.v.w.		1·80	1·79				602	1·74
d_{13}	v.v.w.			1·74					

H. *White sulphur*[8]

The study of white sulphur which had hitherto been regarded as amorphous was very interesting and it led to quite unexpected results.

A quantity of redistilled sulphur monochloride (S_2Cl_2) prepared by passing perfectly dry chlorine over molten sulphur,[17] was hydrolysed by the addition of a sufficient quantity of distilled water. At first a sticky mass was formed which subsequently turned into a hard greyish solid substance known as white sulphur.

A thoroughly powdered specimen was examined by X-rays. The nature of the diffraction pattern (Fig. 3) showed clearly that white sulphur consisted of minute crystals, the perfection of which is in no way inferior to that of carefully recrystallised S_α from a solution in CS_2. In order to form an idea about the size of the crystals in white sulphur, a very thin film of white sulphur was prepared. During the hydrolysis of S_2Cl_2, when a gummy soft mass was formed at a certain stage, a small quantity of it was pressed between two photographic glass plates to sufficient thinness. The soft film so obtained was subsequently treated with water until the hydrolysis was complete. This film was exposed to X-rays and the diffraction pattern bore a point-to-point resemblance to that of the powdered specimen. It thus became evident that the crystals as they grew during the process of hydrolysis were extremely small, so that a complete random orientation of the lattice-planes relative to the X-ray beam was possible. The simultaneous presence of sharpness and uniform intensity in the diffraction rings clearly shows that the extension of the crystal grains in each direction lay within the range 10^{-3} to 10^{-5} c.m.[13]

TABLE III.

Spacing × 10^8.	Intensity.	White sulphur	Spacing × 10^8.	Intensity.	White S. after heating.	Intensity.	Recrystallised sulphur.
d_1	m.s.	4·50	d_1	m.s.	5·66	m.s.	5·66
d_2	s.	4·02	d_2	v.s.	3·85	v.s.	3·84
d_3	s.	3·56	d_3	s.	3·45	s.	3·45
d_4	s.	3·07	d_4	s.	3·09	s.	3·14
d_5	v.w.	2·71	d_5	m.s.	2·84	m.s.	2·84
d_6	v.w.	2·30	d_6	w.	2·64	w.	2·64
d_7	w.	2·10	d_7	v.w.	2·11	v.w.	2·12

Measurements of diffraction rings of white sulphur revealed that the crystals of white sulphur have a structure quite different from that of S_α. The table (III) shows the values of the Bragg-spacings of white sulphur and their relative intensities on an arbitrary scale.

White sulphur or S_ω* is a highly stable crystalline variety of sulphur, just like S_α at ordinary temperature. It does not pass to the α-form slowly or rapidly at the room temparature, like the monoclinic variety ($S\beta$). We have examined S_ω after one year since its preparation and have found that the whole of it still remained insoluble in CS_2 and produced a system of diffraction rings exactly similar to those obtained in the case of a freshly prepared specimen.

It, therefore, appears that sulphur may exist at the ordinary temperature in two distinct crystalline states, namely, S_α and S_ω and both are highly stable. The mode of its preparation alone determines the state it assumes. It may, of course, be possible that one of the crystalline states is unstable. The rate of transformation of the unstable variety is extremely slow and can not easily be detected. For, it appears impossible that one and the same substance may exist in stable equilibrium in two different configurations (S_α and S_ω) under the same physical conditions. Sometimes impurities present in the mother substance influence its structure in such a way as to totally transform it. But at the present stage when the experimental evidences are quite meagre, no satisfactory conclusion can be arrived at about the real nature of S_ω.

4. THE TRANSITION OF S_ω INTO S_α AT HIGH TEMPERATURES

A quantity of white sulphur was heated at a temperature of about 88°C for 36 hrs. and was analysed by X-rays at the room temperature. A pure S_α-pattern (Fig. 1) was obtained and the rings were quite sharp and narrow. The process of heating therefore, had completely modified the structure from the ω to the α-type. The α-modification so obtained was found to be quite stable at the ordinary temperature, as one should expect, and no sign of its reconversion was ever noticed.†

5. TRANSITION OF S_α INTO S_β BELOW THE MELTING POINT

As mentioned before (sec. 1b), we know from chemical literatures that orthorhombic sulphur is the only stable crystalline variety at the ordinary temperature,

* As white sulphur possesses a distinct crystalline structure different from that of S_α and S_β, we think it proper to represent it by a different symbol S_ω.

† The process of conversion of S_ω into S_α has recently been studied in greater detail. The results seem to throw a new light on the nature of S_ω and will be published in a future paper.

but it becomes unstable above 95°·5C. At this temperature and above it, orthorhombic sulphur passes slowly into a second crystalline phase ($S\beta$) belonging to the monoclinic type. With a view to study the transition phenomenon, a cell of finely powered orthorhombic sulphur was prepared and was maintained at a temperature of about 100°C during the exposure. But the photograph failed to furnish any evidence for the said transition phenomenon. A large number of exposures were made at temperatures varying between 90°C and 100°C and in every case, the pattern appeared highly irregular owing to the appearance of spots or dots, and long streaks (Figs. 12, 8 and 9). In most of the photographs no ring could be traced and the plates were full of blurred, or sharp spots. This peculiar phenomenon, although baffled our present endeavour, suggested another line of study and the results have been embodied in the next section (6). There we have come to the conclusion that the peculiar changes in the diffraction patterns are not at all associated with the transition phenomenon but are connected with the growth of the crystal size.

As it was found that the specimen when heated during the exposure, always exhibited dots, streaks, etc., and gave no idea of the transition from S_α to S_β, another method of enquiry was adopted. Thus in one of our experiments, the specimen was heated continuously to 100°C for about three days, which was long enough for the conversion of S_α into S_β. A small quantity of the heated specimen was quickly powdered* in a mortar and placed in the proper position for exposure at the room temperature.

Each exposed sample was replaced by a freshly prepared one after one hour. Though S_β is unstable at the ordinary temperature, yet the transformation of S_β into S_α does not take place very rapidly.[18] This only produced a ring system exactly resembling that of rhombic sulphur (S_α). Similar experiments were performed with sulphur heated to higher temperatures (up to 100°C) for longer periods, and with quicker alteration of the exposed specimen but in no case any change in the ring system could be detected.

In another series of experiments, needles of monoclinic sulphur were first prepared by cooling molten sulphur in a crucible.[18] Very fine shining needles projecting inwards from the walls of the vessel were obtained. Some of them were crushed in a mortar and examined at the room temperature. In this experiment the specimen was also changed every one hour during the exposure. The photograph showed exactly a S_α-pattern as mentioned in the previous paragraph. One is thus forced to the conclusion that either the period of conversion of S_β to S_α is shorter than the accepted period, or the process of powdering completely influences the conversion. From these experiments, no definite

* The powdering is essential for the appearance of continuous rings on the plate. If the specimen is first heated for a long time and then cooled to the room temperature, it only shows dots, streaks, etc. (see Sec. 6).

conclusion could be arrived at regarding the transition temperature of S_α to S_β in the solid state. Further experiments are being conducted to elucidate this point.

6. SULPHUR AT HIGH TEMPERATURE, BUT BELOW THE MELTING POINT

It has been mentioned before (Sec. 5) that the ring system in the diffraction patterns of sulphur becomes very irregular when the specimen under examination is maintained at a high temperature during the exposure. With a view to study the phenomena systematically, several photographs were taken not only at different temperatures but also at each temperature the specimen was heated for different periods before the actual exposure. As a result, we have noticed that the special features characterising the patterns obtained at temperatures lying between 80°C and 110°C are (*a*) the discontinuity of the rings, (*b*) the appearance of asterism, *i.e.*, radial streaks, and (*c*) the appearance of a large number of sharp intense spots arranged irregularly on the plate. We have further observed that the nature of the pattern at any definite temperature depends again on the total period for which the specimen of sulphur is heated before the actual exposure.

As for example, three distinct stages of changes in the pattern were detected at 104°C. The first photograph (Fig. 12) was obtained with a specimen which was heated only during the period of exposure which was about ten hours. The figure shows very clear signs of asterism, specially in the central region of the photograph. The second stage of the pattern is illustrated in figure 8, where the specimen was heated for about thirty hours at 104°C before the exposure and the same temperature was maintained throughout the exposure. Here the asterism is less marked and the rings are distinctly broken or dotted in appearance (several intense spots appear on the plate) and all of them are not clearly separated. In the next photograph (Fig. 9) which was taken with the specimen heated for a period of sixty hours at 104°C, we see the last and the final stage of the pattern. This state persists for further periods of heating the exposed specimen, and it is characterised by the extreme sharpness of the intense spots on the photograph. They are now quite separated from one another and though they are arranged quite at random over the whole surface of the plate, yet they strongly resemble the spots in a Laue pattern in external appearance. The phenomenon of asterism persists up to the second stage but is never observed in this final stage.

Exactly similar experiments were repeated at different temperatures. We have noticed that the phenomenon of asterism is observed in a marked degree at higher temperature but it also appears at a temperature as low as 80°C, where it is very much less pronounced. Below 75°C we have not been able to detect

any asterism, although the grainy appearance of rings or the appearance of blurred intense spots is clearly revealed. At these lower temperatures again, the rings never disappear totally but only they are weak, and a number of spots appear on the plates. Some of the spots lie on the rings no doubt, but most of them are arranged in a disorderly manner. Recently we have observed these sharp spots even in the patterns of specimen at the room temperature 30°C, which was powdered a few days before the actual exposure.

It is quite evident from the above experiments that there must have been some sort of change taking place in the crystal texture of the powdered grains, when they are subjected to some heat treatment at high temperature. The first observation of the above peculiarities in the diffraction photographs at high temperatures was made at 100°C. This temperature was chosen with a view to study the phenomenon of enantiotropic transformation of sulphur, which is generally believed to take place above 95°·5C (see Sec. 5). The appearance of asterism in the photograph at this temperature and also in others taken subsequently at various temperatures suggested that this effect might be due to some curvature of the lattice planes of the minute crystals in the powder, caused by the well known transformation strain which is produced homogeneously throughout each crystal at the time of transition from one crystalline phase to the other.[19] The increased prominence of asterism with the increase of temperature generally supports the view. For a higher temperature in the case of enantiotropic structural transformation is equivalent to a greater force producing the strain. Moreover the total disappearance of asterism at lower temperatures gives further support of this view. But if this transformation strain is really responsible for asterism, then such transformation ($S_\alpha \longrightarrow S_\beta$) can also take place at so low a temperature as 80°C where the phenomenon is clearly observed. But the existent literatures on sulphur do not support this latter point. According to them the structural transformation of sulphur does not take place below 95°·5C. D. Gernez [20] goes even further and according to him the transformation of S_α into S_β can not take place below the melting point, unless S_α is already admixtured with a quantity of S_β and even in that case the transformation takes place at 97° 6C. E. Mitscherlich [20] was of opinion that the transition point lies in the proximity of the melting point of S_α.

Further if we assume that the transformation of S_α into S_β is possible even at these lower temperatures, still there are certain difficulties which are not clearly understood from this point of view. For example the strains produced during the process of structural transformation cannot account for (*a*) the discontinuity of the rings and (*b*) the appearance of innumerable sharp spots on the plates at the final stage of heating the exposed specimen. We shall see below that all the observations on sulphur here described find satisfactory explanations on the basis of the idea of growth of crystal-size at high temperatures.

To test the validity of the above idea we performed another experiment and results have confirmed this view. A quantity of finely divided sulphur was made into a thick paste with the help of collodion and a mixture of ether and alcohol. Allowing the paste to spread over a plane glass plate a film of sulphur-in-collodion was obtained. Inside the film, fine grains of sulphur remain embedded in the solid medium of collodion and are thus debarred from coming in contact and uniting together to form bigger crystals at higher temperatures. A suitable portion of the film was exposed at 104° C in the usual way and the pattern (Fig. 10) did not exhibit any peculiarity observed in the previous experiments. The nature of the pattern at 104° C was exactly similar to that at the room temperature.

7. THE PROCESS OF CYRSTAL GROWTH IN THE POWDERED GRAINS OF SULPHUR AT HIGHER TEMPERATURES

Evidences are now rife for the growth of bigger single crystals at sufficiently high temperatures from the polycrystalline aggregates of metals [21] The acceleration of crystal growth at higher temperatures has led to the idea that the increased thermal energy possessed by the molecules of the crystals in the form of kinetic energy, causes an increase of mobility of the molecules.[21] This increased mobility is essential in the building up of bigger structures. For a small unit of crystal powder which we may assume to consist of a single crystal having some minute surface defects due to powdering, must be associated with other molecules or smaller units in the right positions and for this purpose even the molecules lying in the most favourable positions must possess sufficient freedom to move, so that their migration into the exact positions in the lattice may be possible.

Let us now consider a single grain which has a large number of similar immediate neighbours. The proper union between them resulting in a bigger single crystal must involve cementation of one unit with the other through faces which are crystallographically similar. When two such faces of the two neighbouring grains closely approach each other with their directions approximately parallel, a very favourable condition is created for their union into a bigger unit. The semi-crystalline layers of molecules covering each member of the growing particles will now bring about the union, forming themselves a sort of bridge-layer between them. This cement layer plays a very important part in the process of crystal growth in polycrystalline masses.[21] In the first stage they remain in a more or less amorphous or semi-crystalline condition having a tendency for molecular alignment which is greatly helped by the increased mobility due to the rise in temperature. In the primary stage of development the grown-out-structure will behave as a highly imperfect single crystal owing partly to the approximate

parallelism of the uniting faces and partly due to the presence of the compromising semi-crystalline cement layer.

But as the period of heating continues these highly imperfect structures, on the one hand, associate themselves with other favourably oriented grains and thus grow into still bigger units while, on the other hand, the cement layer acts in such a way as to eliminate the defects present between two neighbouring faces. The gradual improvement of the order of perfection of the crystal is effected by the slow alignment of the molecules in the cement layer in a way demanded by the adjoining crystal faces. We may now imagine that, of the two adjoining faces, only one is absorbing the molecules available in the cement layer. This causes the consumption of the whole layer present at the beginning of the process. But really until the whole structure becomes truly perfect (certainly an ideal perfection is never realised) the boundary layer will never be totally absent. For as the layer loses one molecule by the process of alignment, another may be substituted there from the neighbouring face of the other unit, which is supposed to be inactive. Thus practically there is a continuous transport of molecules from one of the adjoining faces to the other, and the semi-crystalline layer is always present as a dynamically stable intermediate stage in the formation of big single crystals.

In an ideal condition when there are no impurities accumulating on the boundary layers [22] retarding the function of the cement layer and when the rate of growth is fairly slow, we may expect an ideally perfect crystal by a long continuation of the process. But this ideal is hardly realised in practice and ultimately we are satisfied with a mosaic structure, which for all practical purposes serves as a good single crystal. Before actually interpreting our results with sulphur at high temperatures, we would like to present a picture of the diffraction phenomena including asterism as may be observed in the case of a crystal in its various stages of changes. Let us consider the diffraction pattern from a polycrystalline mass consisting of a number of single crystals distributed quite at random. In this case the pattern will evidently consist of a very large number of sharp Laue spots arranged in a disorderly manner.* If the constituent single crystals of the polycrystalline mass be now so fractured, as to be sub-divided into smaller units having their corresponding faces only slightly deviated from their original positions of accurate parallelism, the pattern will no longer exhibit any sharp spot, but will consist of radial streaks. For, just as the image of a luminous point formed by reflection from a plane mirror assumes the shape of a long streak (strictly a

* The number of crystals actually taking part in the diffraction should be very small such that it does not exceed, say, about 50. G. I. Clark has photographed the pattern due to polycrystalline aluminium sheets of various degrees of crystalline grain-size. The patterns of sulphur in the final stage of heating exactly resemble those of aluminium taken by Clark.—

[22] See Bragg and Bragg, "The Crystalline State," Vol. I, p. 191.

highly eccentric ellipse), if the mirror is rotated in space with the normal lying within a small solid angle round its original position, so the Laue spots formed by reflection from the faces of the slightly orientated constituent units of the imperfect crystals will be elongated into streaks. Again, if these units are further disturbed or the diffracting units are powdered, so that the powdered grains are sufficiently small and their orientation is quite random, familiar Debye-Scherrer rings appear on the photographic plate.

The case of sulphur at high temperatures is very similar to the above case of the polycrystalline mass but the procedure is just the reverse. Here we start with a powdered specimen of sulphur which produces well defined Debye-Scherrer rings. With the increase of temperature, the minute single crystals begin to grow in size. In the first stage of the growth, the grown out structures remain highly imperfect, for the crystallographically similar faces of the component units are slightly deviated from one another with the results that continuous rings disappear and streaks or asterism come out prominently on the plate. With lapse of time, however, the imperfections of the grown out crystals gradually disappear and ultimately we arrive at a stage where the crystal grains become sufficiently perfect and large to produce sharp Laue spots of complicated nature. No streak may appear in this case.

In connection with the picture represented here above the growth of the crystal size, we like to reiterate the case of solidified plastic sulphur or the other types of sulphur which are not soluble in carbon disulphide (Sec. 3 F). The sizes of the crystals in these modifications are very small as they produce quite continuous rings without any further powdering the sample. This state is preserved until it is heated to a high temperature. It has been mentioned before that there is a strong evidence that a layer of SO_2 gas is formed and adheres to boundary surface of the grains of the insoluble sulphur modifications and this layer separates one unit from the other. If the sulphur molecules on the boundary possess sufficient kinetic energy to penetrate the SO_2 layer, then only growth may take place.[22] At ordinary room temperature * evidently these sulphur molecules are not sufficiently mobile to pierce through the layer of SO_2 and thus bring about the growth in a manner discussed before. But as the temperature is raised, the layer of SO_2 gas is removed and then the growth commences in the usual way.

8. LIQUID SULPHUR (FIG. 10)

The work of Blatchford[12] on liquid sulphur at various temperatures has already been mentioned before (Sec. 1(*d*)). His investigation was carried out

* Distinct evidence of the growth of the sulphur powdered crystals which are soluble in CS_2 has been found even at the room temperature.

within the range of 130°C to 210°C. The arrangement only provided a small resolution and thus he observed only one diffraction band (Table IV) in the case of molten sulphur. With a narrower slit (0·4 m.m. diameter whereas the other author used a slit of 1·5 m.m. diameter) and a greater resolution two well defined rings have been observed The spacings are recorded below :

TABLE IV.

Spacing × 10^8.	Intensity.	114°C.	119°C.	128°C.	Blatchford[12] (130°C)
d_1	w	4·96	5·14	4·90	$3·68 \pm ·01$
d_2	S	3·42	3·51	3·45	

We confined our attention purposely below 130°C (the lowest temperature of Blatchford's experiment) with a view to study any structural difference between molten S_α and molten S_β Rhombic S_α and monoclinic S_β sulphur were prepared in the usual way, and the liquid structure was examined just above the melting point, namely, 114°C (for S_α) and 119°C (for S_β) but no difference in the spacings calculated by the Bragg-relation could be detected.*

9. SULPHUR AT LOW TEMPERATURE

Preliminary investigation on S_α was carried out at the temperatures of CO_2 snow, mixture of CO_2–snow and ether, and liquid oxygen. The powdered substance appeared perfectly white even at the temperature of CO_2 snow. The rings appeared sharper and better defined but hardly any difference in the structure could be detected.

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* Recently further examination of liquid sulphur has been continued and the detailed result will be published in the next part.

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